Journal of Physics: Conference Series **98** (2008) 032009 doi:10.1088/1742-6596/98/3/032009

Electrochemical control over disintegration of solid solutions of Mg in Al

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Abstract. The non-equilibrium variant of the EMF method under continuous temperature decrease at a rate of 5-7°C per minute was used for the first time to study the thermodynamic properties of Mg solid solutions in Al. This allowed to establish a valid relation between the abrupt change of the potential of Al-Mg alloy with Mg content 20-30 mol. % at 370-380°C and the disintegration of the solid solution formed at 450°C.

1. Introduction

The formation and disintegration of solid solutions, which allow to improve considerably the exploitation characteristics of products, are the basis of the thermal treatment of metal alloys. The basic methods of solid solution disintegration control are X-ray phase analysis and testing of mechanical properties of the products exposed to the thermal treatment. We consider the possibility of electrochemical control over solid solution disintegration using the non-equilibrium variant of the EMF method. We have already obtained information of the thermodynamic characteristics of homogeneous and oversaturated solutions of zirconium in liquid bismuth, measuring EMF of amalgam galvanic cells under continuous temperature variation [1]. The results obtained are similar with equilibrium measurements of the homogeneous solutions at cooling rates of 3–10°C per minute.

The Al-Mg phase diagram is the basic one for the industrial alloys in which Mg contents vary widely. The β phase (the compound of Mg_2Al_3), which forms eutectic with solid solutions on the base of aluminum Al+β at 450°C [2], is the strengthening phase in these alloys.

Since Mg solubility in solid Al decreases markedly with the decrease of temperature, the processes of formation and disintegration of oversaturated solid solutions are possible for the alloys in this system. The object of this research is to consider such processes using electrochemical methods.

2. Experimental

A–85 aluminium and Mg–90 were used to prepare the Al–Mg alloys. K, Li chlorides and carnallite dehydrated and preliminary melted were used to prepare an electrolyte. The experiments were carried out in the atmosphere of purified argon. The structure of the electrochemical cell is shown in figure 1.

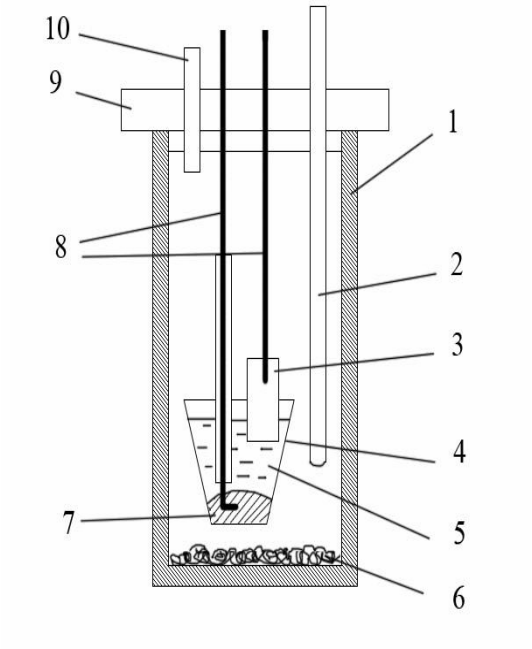

Figure 1. Electrochemical cell.
1. Steel retort; 2. Thermocouple; 3. Magnesium;
4. Crucible; 5. Electrolyte; 6. Mg–powder;
7. Al–Mg alloy; 8. Mo – wires; 9. Lid;
10. Air pipe-bend.

The EMF of the galvanic element

$$\text{Mg / KCl–LiCl+25 mol.\%}MgCl_2\text{ / Al+20 at.\%Mg} \quad (1)$$

was measured in the temperature range from 600 to 320°C, the content of Mg in Al was 20–30 at.%. The alloys were prepared by alloying the components directly in the argon filled vacuum–processed cell under dehydrated melted electrolyte to provide the initial alloy composition maintenance. Upon reaching EMF equilibrium value at the highest temperature when within half an hour the change of its value was not more than 0.2–0.3 mV (it took from 1 to 2 hours) the temperature dependence of EMF was measured under continuous temperature variation at a rate of 5–7°C per minute. The temperature dependence of EMF (E=c+d·T) was determined for each area of the phase diagram and the areas were used to calculate the temperature dependence of the Mg activity and its activity coefficient in the Al-Mg alloys:

$$\ln a = -\frac{nF}{RT}E\,; \qquad \ln\gamma = \ln a - \ln x. \quad (2)$$

3. Results and discussion

The area of homogenous liquid solutions (600–550°C) for 20 at.% of Mg, 600–500°C for 30 at.% of Mg, the two-phase area (solid solution of Mg in Al +liquid) 550–450°C for 20 at.% Mg, 500–450°C 30 at.% Mg, and the area of solid solutions and β phase co-existence can be seen on the temperature dependence of the element EMF (1) (figure 2).

For the area of homogeneous liquid solutions our results are in good agreement with the previous ones [3]. Since the latter results are given with respect to liquid Mg, a correction is made taking into account the changes of thermodynamic functions during the solidification of Mg (ΔH=−9200 J/g at; ΔS=−9.97 J/g at K) [4]. For example, in [3] the temperature dependence of the EMF element (1) with respect to liquid Mg for the Al–Mg alloys containing 30% of Mg is:

$$E, V = 0.016 + 0.0616\cdot10^{-3}\,T \pm 0.0002. \quad (3)$$

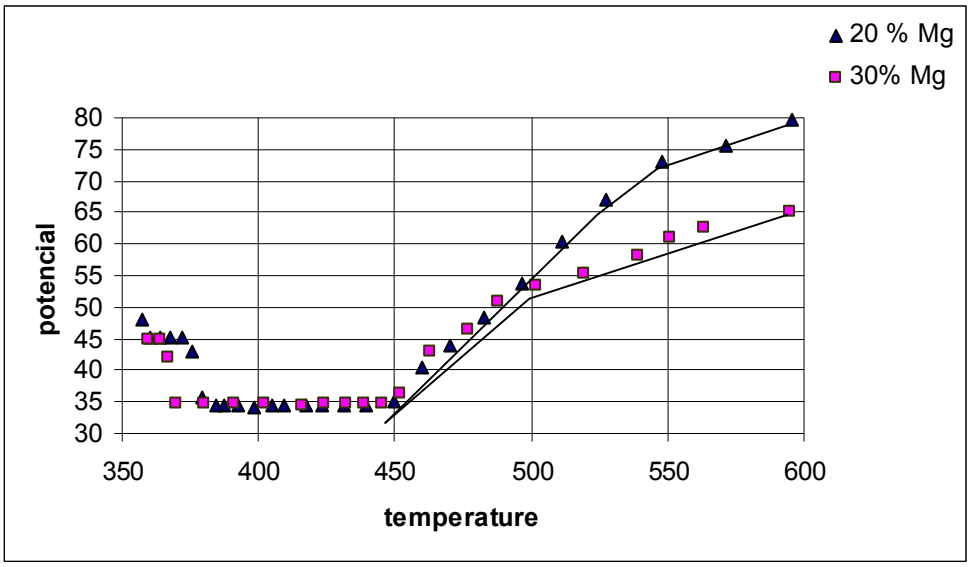

Figure 2. The temperature dependence of the element EMF (1)

With respect to solid Mg equation (3) is transformed into the form:

$$E, V = -0.0308+0.1126\cdot10^{-3}\,T \pm 0.0002;\ E_{873K} = 0.067\ B;\ E_{773K} = 0.056\ V. \quad (4)$$

These data practically coincide with our results:

$$E, V = -(0.0573\pm0.0051)+(0.142\pm0.006)10^{-3}\cdot T\pm0{,}0007;\ E_{873K} = 0.066\ B;\ E_{773K}=0.053\ V \quad (5)$$

We found out the equation of activity temperature dependence and activity coefficient of solid Mg in the liquid Al–Mg alloy of Al+30% of Mg determining (5) from correlation (2)

$$\ln a = \frac{1330\pm120}{T} - 3.29\pm0.14, \quad (6)$$

$$\ln\gamma = \ln a - \ln 0.3 = \frac{1330}{T} - 2.09, \qquad \gamma_{873\hat{E}} = 0.57, \qquad \gamma_{773\hat{E}} = 0.69. \quad (7)$$

Small negative deviations of the activity from the Raoult's law are typical for liquid Mg solutions in Al. The fact is connected with the presence of intermetal compounds in the system.

The EMF temperature dependences of the two-phase alloys (solid + liquid Mg solution in Al) and the activity of the solid Mg in it are the following:

$$E, V = -(0.246\pm0.011)+(0.389\pm0.014)10^{-3}\cdot T\pm0.0015, \quad (8)$$

$$\ln a = \frac{5710\pm255}{T} - (9.03\pm3.2). \quad (9)$$

According to the phase diagram, Mg content in the liquid Al-Mg alloys lying at liquidus line is: under 450°C–0.369; 500°C–0.300; 550°C–0.210 of mole fraction. In the $\ln x - \frac{1000}{T}$ coordinates these data satisfactorily keep within the straight line

$$\ln x = \frac{3342\pm561}{T} - (5.59\pm0.73)\pm0.073. \quad (10)$$

The difference between (9) and (10) gives the temperature dependence of the activity coefficient of solid Mg in liquid two-phase alloys:

$$\ln\gamma = \frac{2368}{T} - 3.44\,, \qquad \gamma_{873K} = 0{,}48\,;\ \ \gamma_{773K} = 0{,}68\,. \tag{11}$$

These values almost coincide with the similar characteristics for the homogenous Al-Mg alloy, with 30% of Mg.

In accordance with (2) Mg solubility in solid Al at 550°C, 500 °C, 450 °C equal to 0.069, 0.128, and 0.189 of mol fraction respectively in the $\ln x - \frac{1000}{T}$ coordinates keep within a straight line

$$\ln x = \frac{5850 \pm 1032}{T} - (9.72 \pm 1{,}34) \pm 0.123\,. \tag{12}$$

The difference between (9) and (12) gives the temperature dependence of the activity coefficient of solid Mg in its solid alloys of the two-phase field under consideration:

$$\ln\gamma = 0.69 - \frac{140}{T}\,, \qquad \gamma_{873K} = 1.7\,; \qquad \gamma_{723K} = 1.64\,; \qquad \gamma_{623K} = 1.56. \tag{13}$$

The activity coefficients of solid Mg in its solid solutions in Al are characterized by small positive deviations from the Raoult's law, the activity coefficient value being the same (1.6±0.1) in wide temperature range (more than 250 K).

The alteration of the potentials with the temperature is going stepwise in the field of the existence of solid phases (solid solution + β). In our opinion the abrupt change of the potential is due to oversaturated solid solutions disintegration. The solutions containing 18.9% of Mg and formed at 450°C disintegrate at 370–380°C. Supercooling reaches 70–80°C, and the degree of oversaturation reaches 1.5. The 0.010 V potential alteration corresponds to the mentioned oversaturation at 380 °C. It is well agreed with the value determined experimentally, that is 0,010 V. The disintegration of the solid solutions at 370–380 °C confirmed the transitory potentials shift at this temperature to the range of values corresponding to the β and γ phase co-existance. Such local oversaturation appeared to be possible owing to Mg forming when the solid solution disintegrates.

4. Conclusions

- The non-equilibrium variant of the EMF method was used to confirm the thermodynamic characteristics of Al-Mg liquid solutions and to study the characteristics of Mg solid solutions in Al for which small positive deviations of the Mg activity from the Raoult's law have been determined. The value of the Mg activity coefficient is practically constant (1.6±0.1) in wide range of temperatures and concentrations.
- The connection between abrupt change of the potentials by 0.010 V at 370–380°C and disintegration of solid solution of Mg in Al, forming at 450°C, has been proved.

References

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